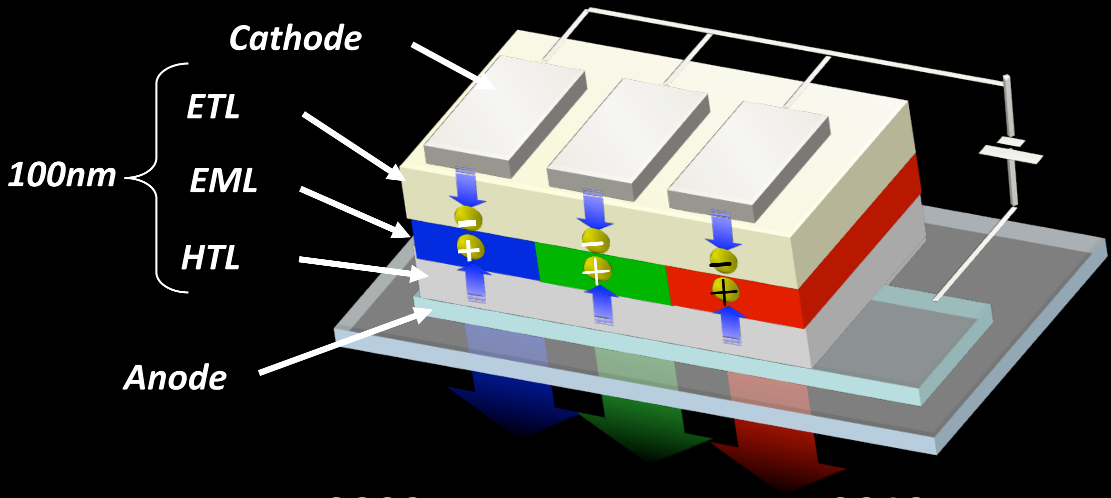
High Performance TADF for OLEDs

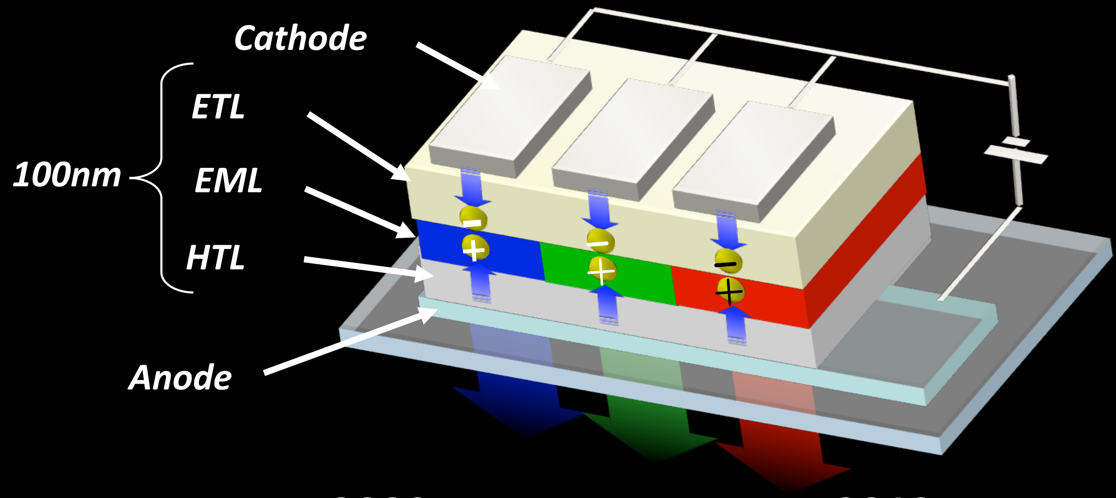


1987~	2000~	2012~	2014~
1st Generation Fluorescence IQE~25%	2nd Generation Phosphorescence IQE~100%	3rd Generation Delayed Fluorescence IQE~100%	3.5th Generation Hyper Fluorescence IQE~100%
		TADF	TADF + Fluorescence

DOE SSL R&D Workshop

OPERA research team
KYUSHU UNIVERSITY
Chihaya Adachi
Junji Adachi

OUTLINES



1987~
1st Generation
Fluorescence
IQE~25%

2000~
2nd Generation
Phosphorescence
IQE~100%

2012~
3rd Generation
Delayed Fluorescence
IQE~100%
TADF

2014~
3.5th Generation
Hyper Fluorescence
IQE~100%
TADF + Fluorescence

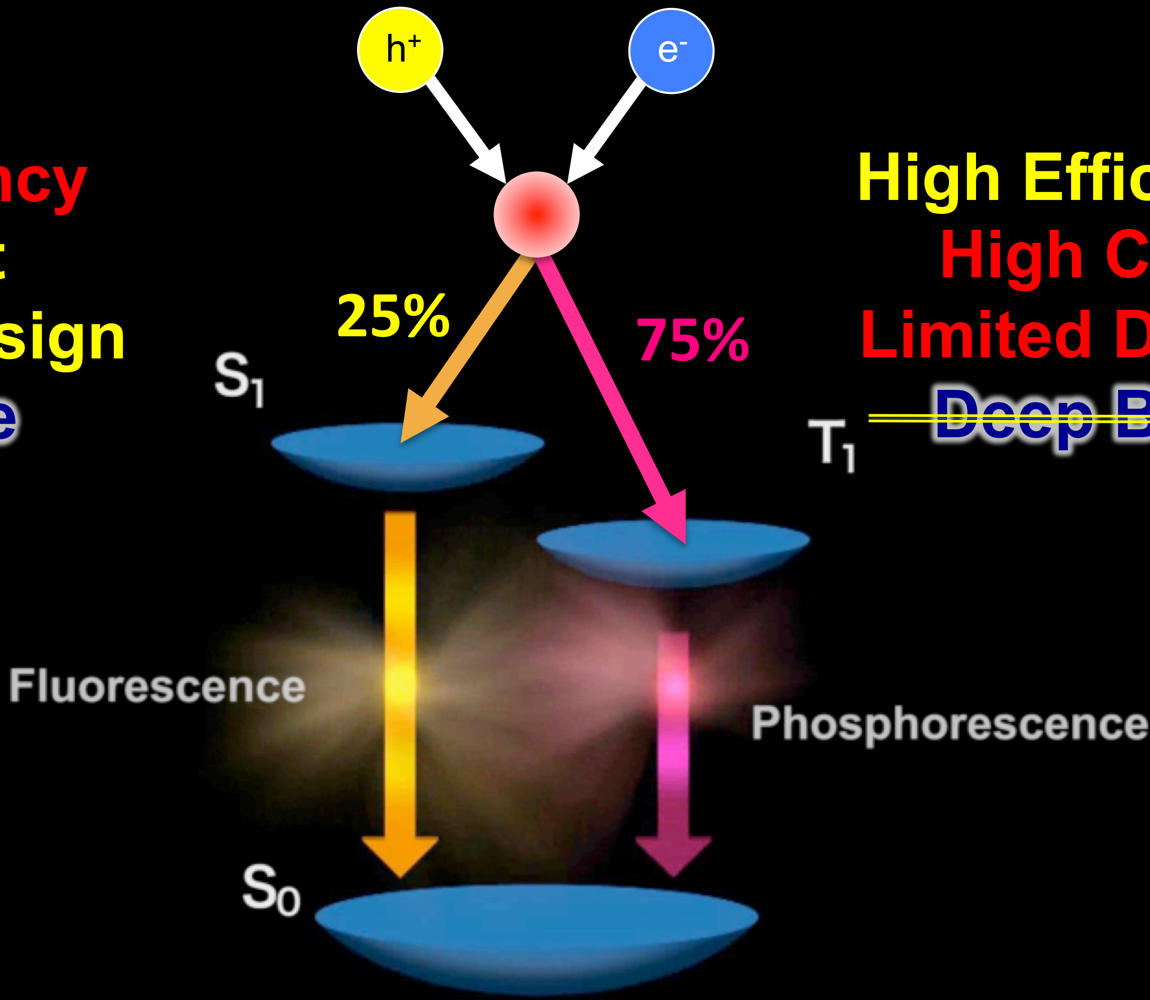
i) Molecular design for high efficiency TADF and their application for OLEDs

*ii) A new route for triplet harvesting using TADF molecules as assistant dopant and fluorescence molecules as emitter (**Hyperfluorescence**)*

iii) Triplet exciton management for reduced roll-off and device stability

Principle of Conventional Emitting Process

Low Efficiency
Low Cost
Unlimited Design
Deep Blue



High Efficiency
High Cost
Limited Design
~~**Deep Blue**~~

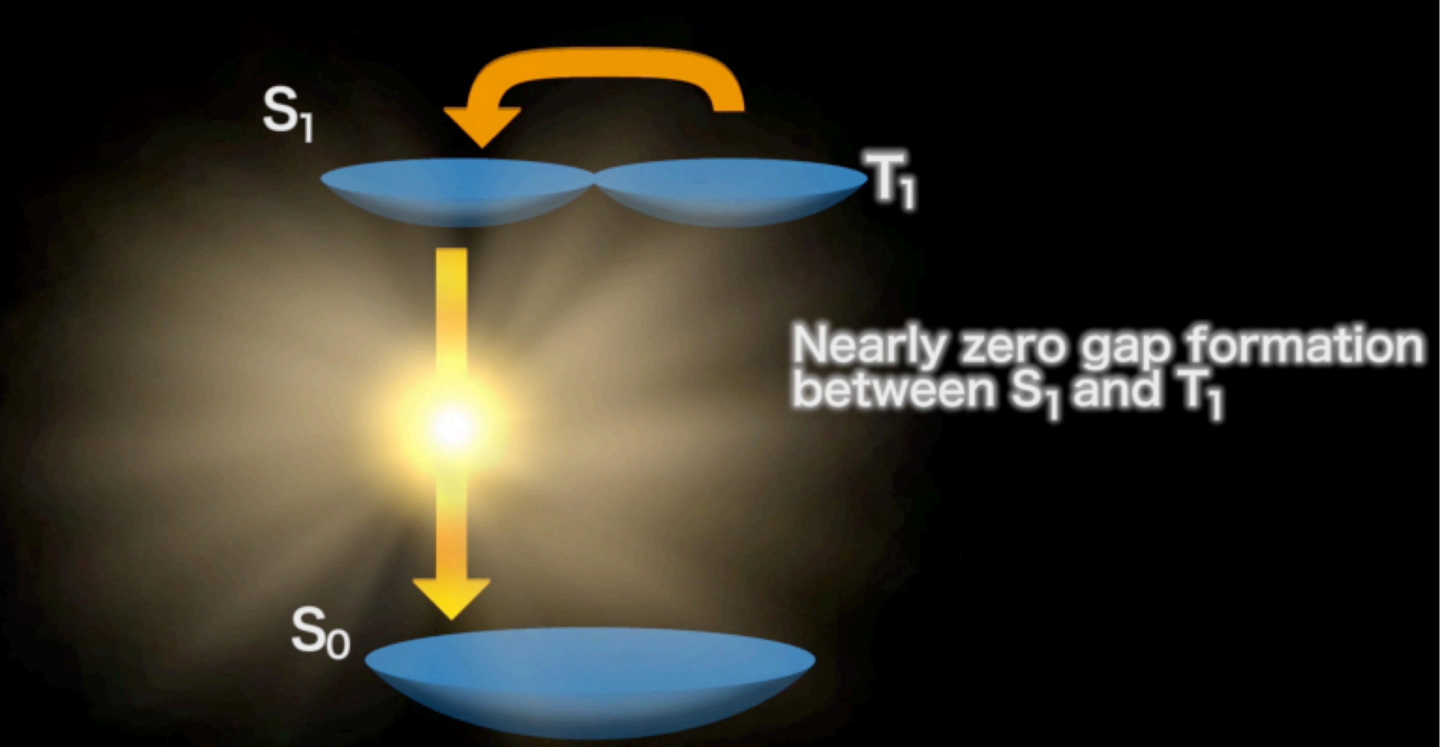
Conventional fluorescence and phosphorescence processes

Principle of TADF

$$\lambda \propto \frac{H_{SO}}{\Delta E_{ST}}$$

First-order mixing coefficient between singlet and triplet states (λ)
H_{so}: Spin-orbit coupling

Larger λ provides larger probability for transition between S_1 and T_1 states.



High efficiency thermally activated delayed fluorescence (TADF) via reverse intersystem crossing (RISC)

KYUSHU UNIVERSITY

Molecular design for efficient TADF

Small: ΔE_{ST}

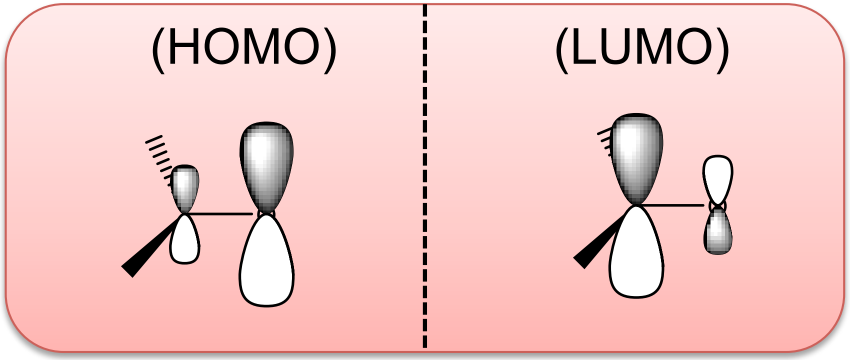
$E_S = (E_H - E_L) + K$

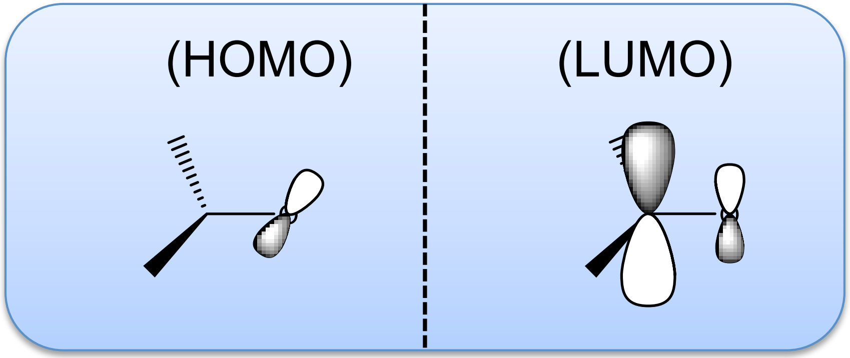
$E_T = (E_H - E_L) - K$

E_H :HOMO Energy
E_L : LUMO Energy
K :Exchange Energy

$\Delta E_{ST} = 2K$

$$K = \iint \phi_L(1)\phi_U(2)\frac{1}{r_{12}}\phi_L(2)\phi_U(1)d\tau_1 d\tau_2$$





・Large ΔE_{ST}

・Small ΔE_{ST}

Moderate Oscillator Strength: f

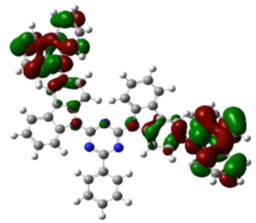
$f \propto \mu^2$ $\mu = \iint \phi_L(1)\phi_U(2) r_{12} \phi_L(2)\phi_U(1) d\tau_1 d\tau_2$

Transition dipole moment

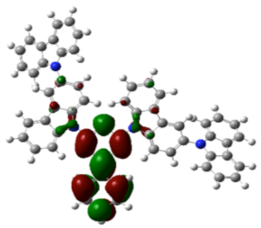
Molecular Design

Donor — X — Acceptor

- ✓ Donor-Acceptor backbone
- ✓ X:Introduction of steric hindrance



HOMO



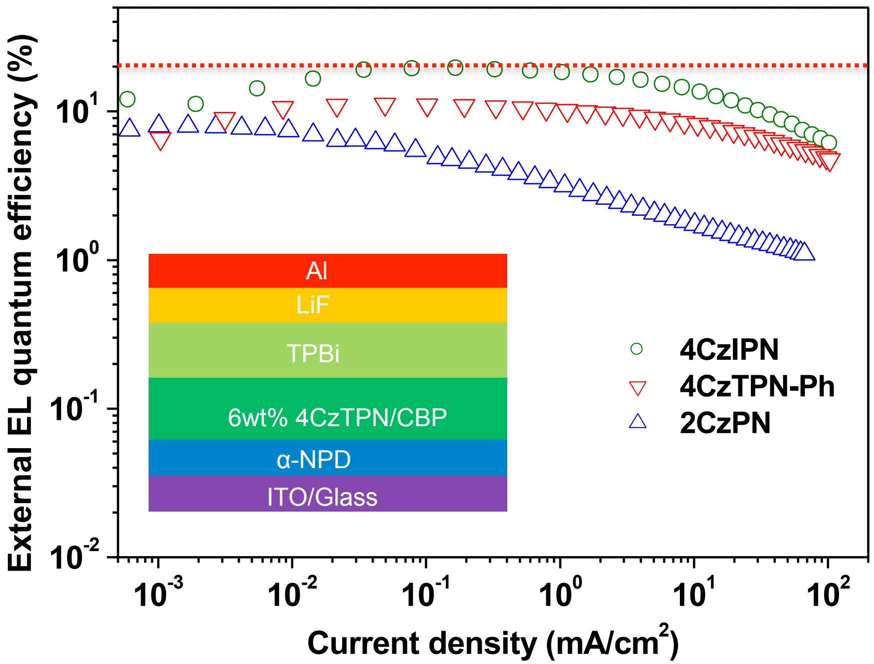
LUMO

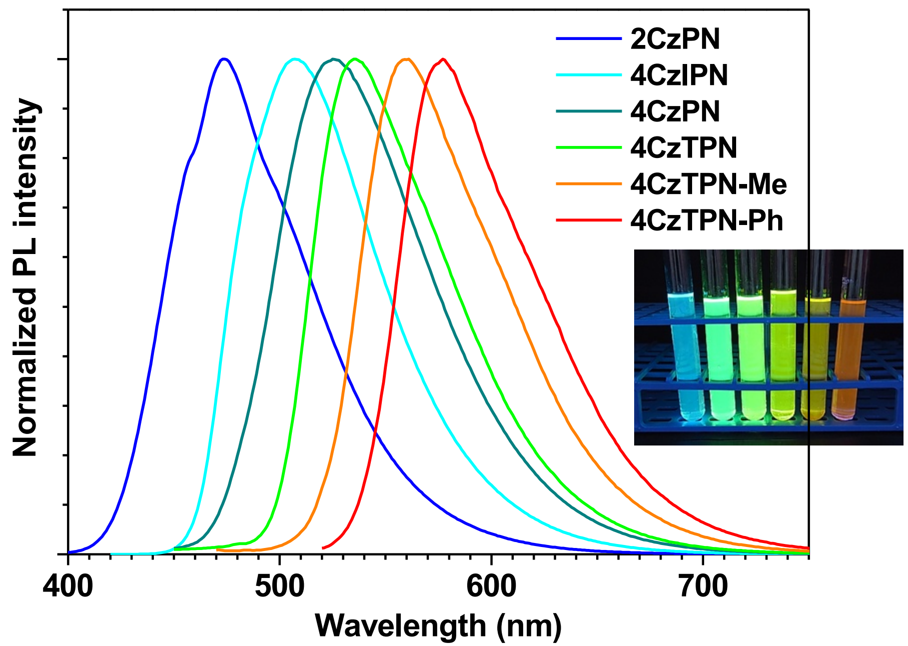
Moderate radiative decay rate with small ΔE_{ST}

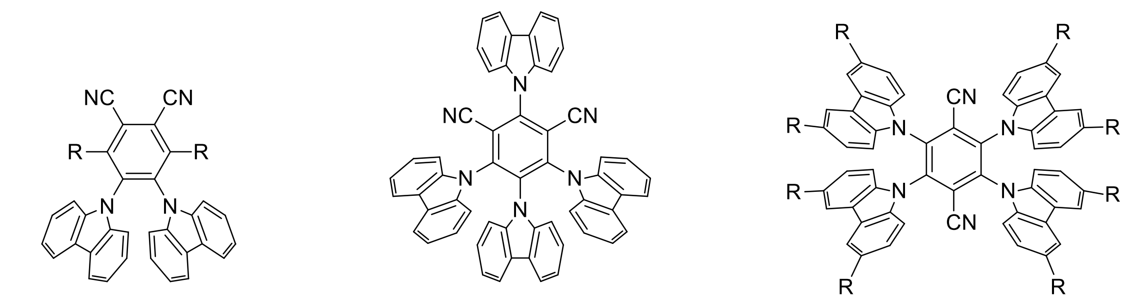
Very high efficiency TADF based OLED (Internal QE~100%)

EQE~20%
(Internal QE: approaching to 100%)

T. Uoyama et al., Nature, 492, 234 (2012)







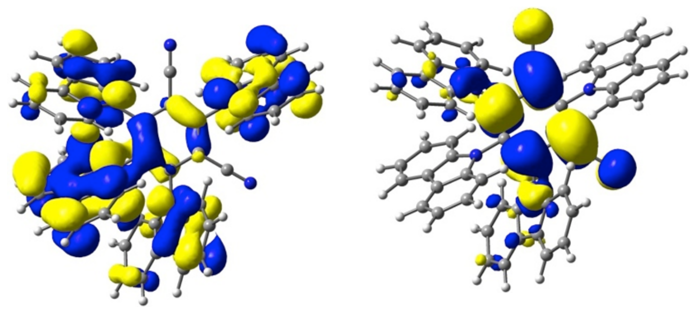
4CzPN: R = carbazolyl
2CzPN: R = H

4CzIPN

PLQY~95%

4CzTPN: R = H
4CzTPN-Me: R = Me
4CzTPN-Ph: R = Ph

Phthalonitrile derivatives



HOMO **LUMO**

DFT (M06-2X/6-31G(d))

Internal QE nearly 100% Blue OLED

nature photonics

nature.com ▸ journal home ▸ advance online publication ▸ article ▸ abstract

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NATURE PHOTONICS | ARTICLE

Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence

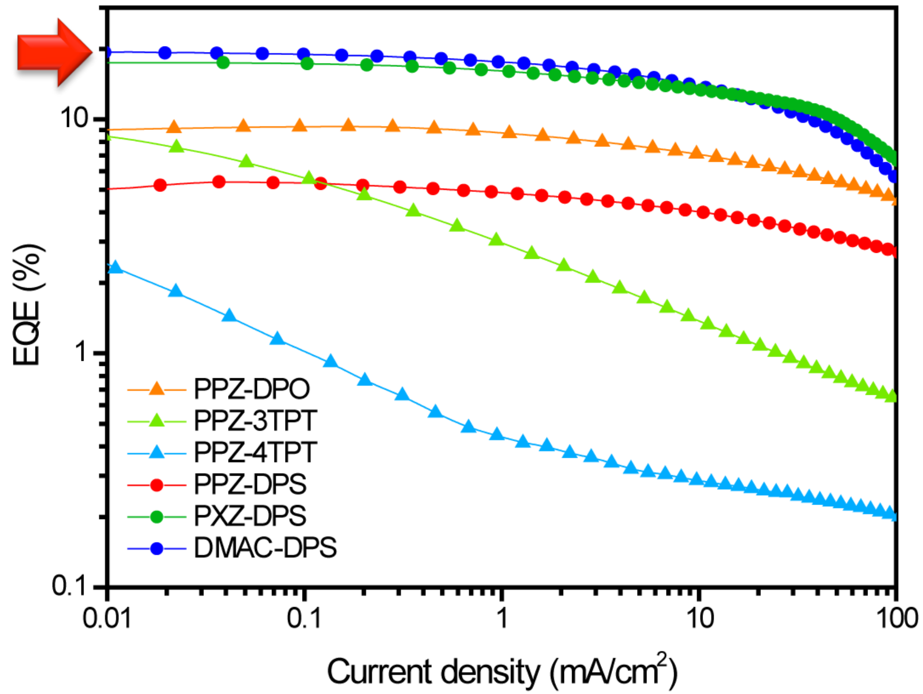
Qisheng Zhang, Bo Li, Shuping Huang, Hiroko Nomura, Hiroyuki Tanaka & Chihaya Adachi

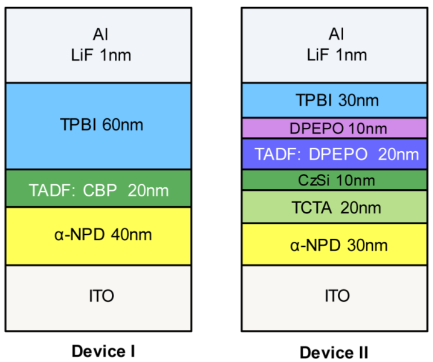
Affiliations | Contributions | Corresponding author

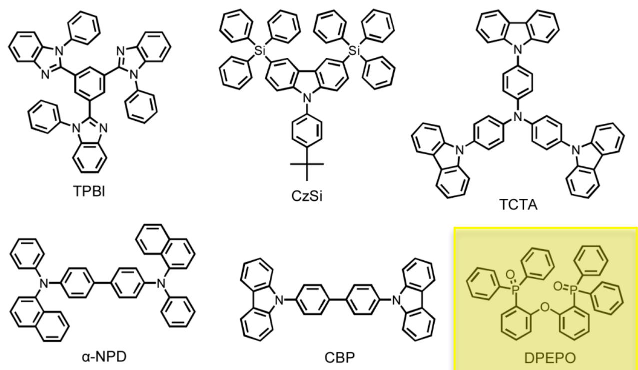
Nature Photonics (2014) | doi:10.1038/nphoton.2014.12

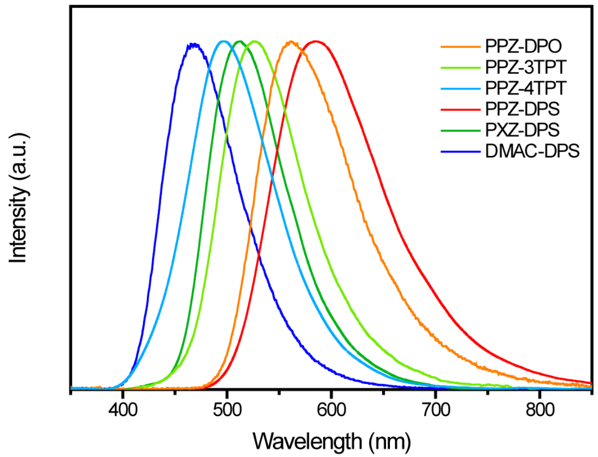
Received 05 August 2013 | Accepted 14 January 2014 | Published online 02 March 2014

EQE20%





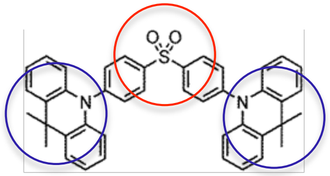




Q. Zhang, et al., Nature Photonics, 8, 326 (2014)

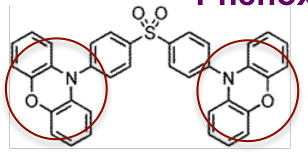
High efficiency blue TADF: Optimization of donor and acceptor units

Diphenyl sulfone (DPS)

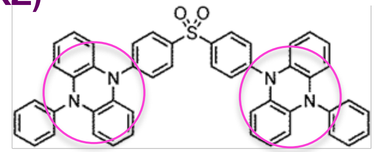


Acridine (DMAC)

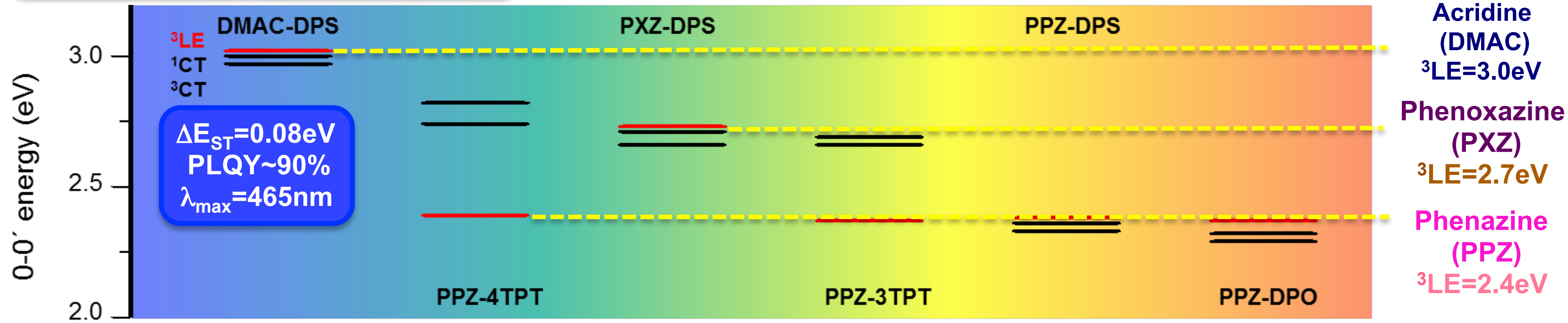
Phenoxazine (PXZ)



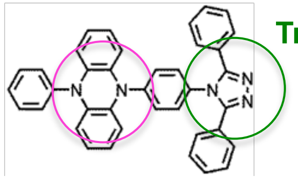
Phenazine (PPZ)



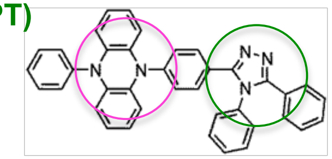
B3LYP/6-31G* level



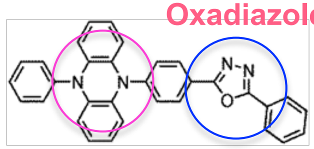
Phenazine (PPZ)

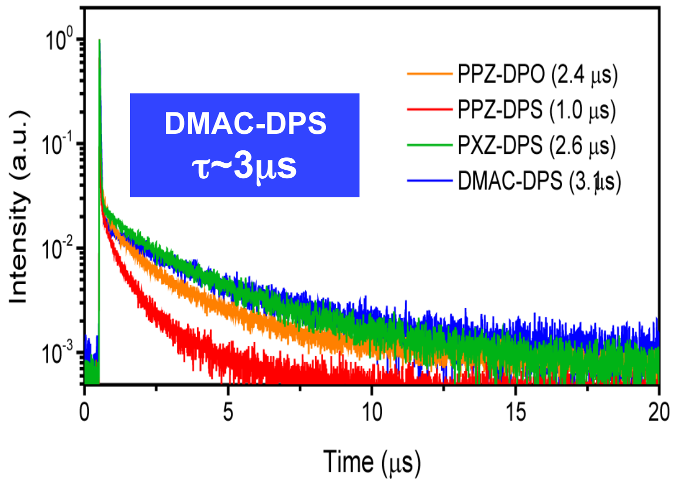


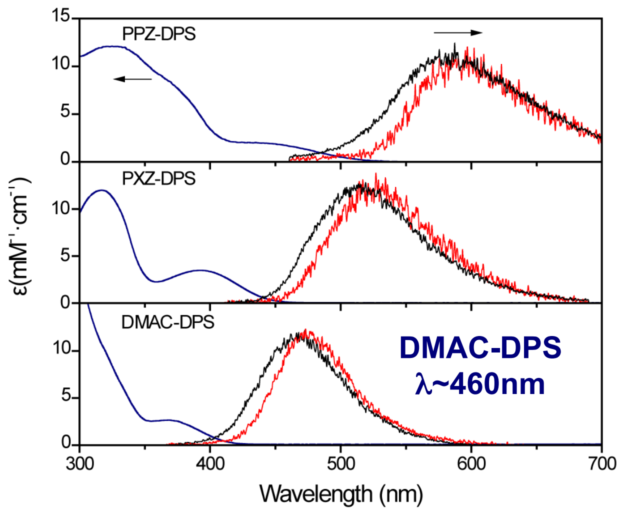
Triazole (TPT)

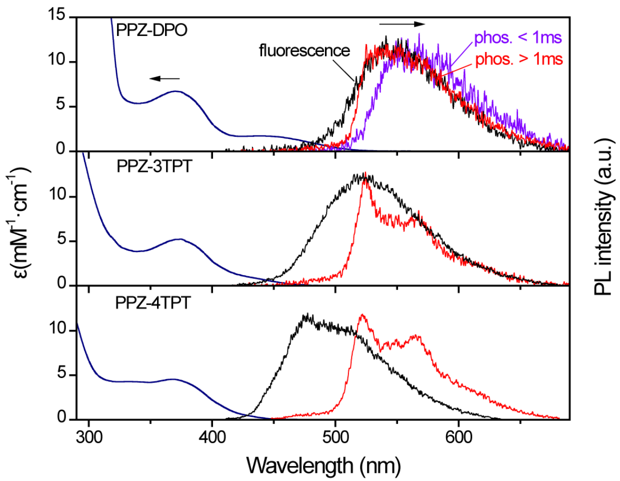


Oxadiazole (DPO)









Red TADF

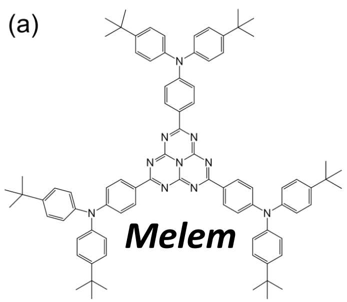
Materials Views
www.MaterialsViews.com
ADVANCED MATERIALS
www.advmat.de

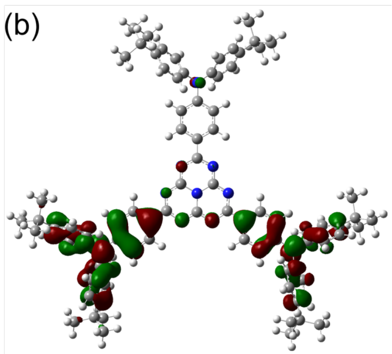
S$_1$-T$_1$ transition is an optically hidden process!

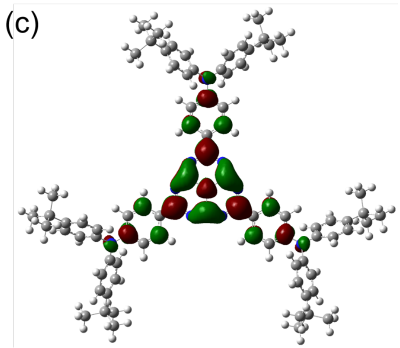
Highly Efficient Organic Light-Emitting Diode Based on a Hidden Thermally Activated Delayed Fluorescence Channel in a Heptazine Derivative

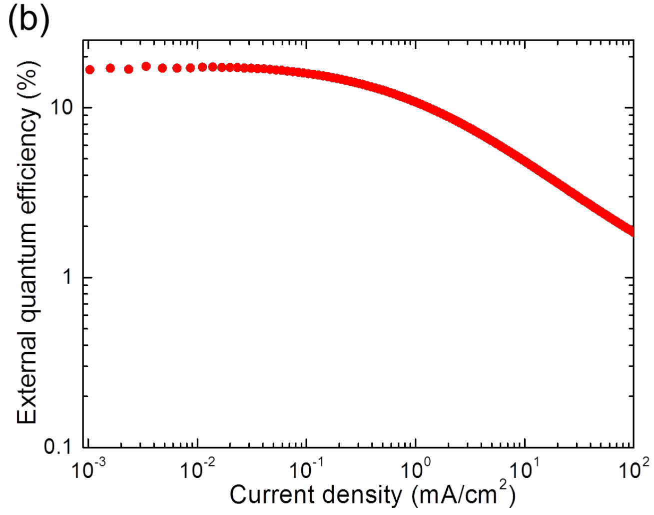
Adv. Mat., 25, 3319 (2013)

J. Li, T. Nakagawa, J. MacDonald, Q. Zhang, H. Nomura, H. Miyazaki, and C. Adachi (CSIRO and Kyushu Univ.)

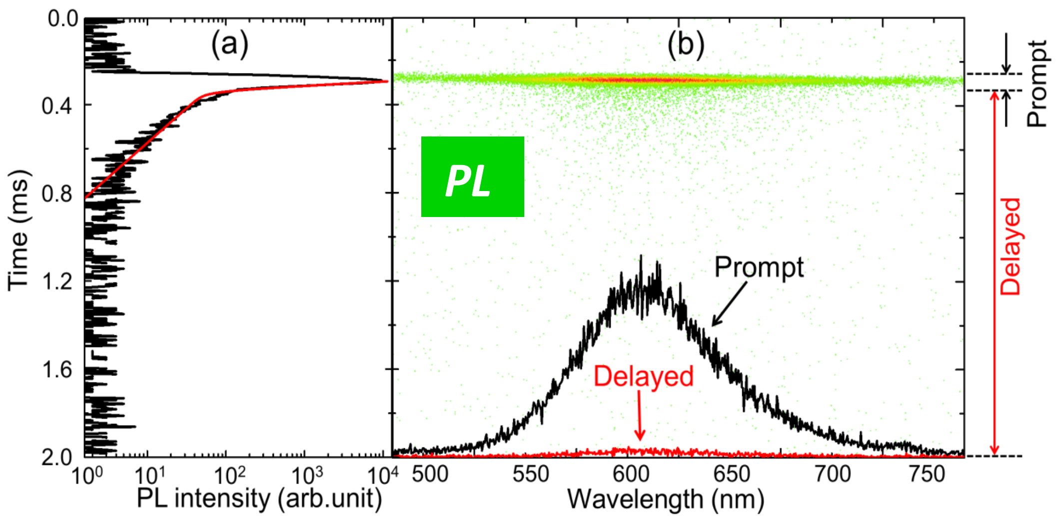


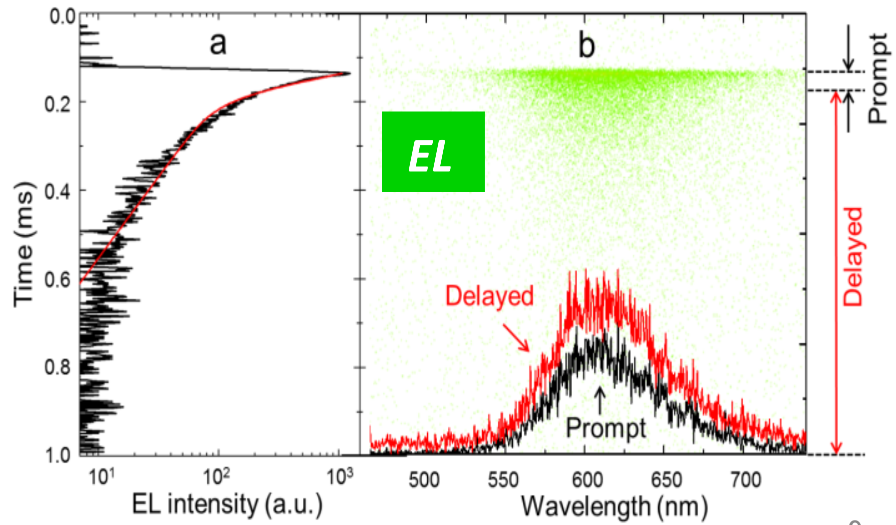






EQE 17.5 ± 1.5%, λ_{EL}~610nm
CIE (0.60, 0.40)

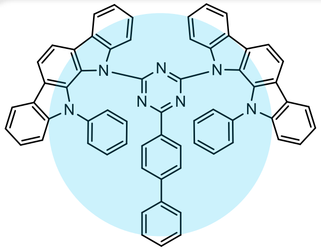




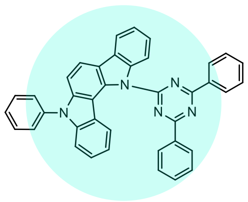
Molecular Design for TADF

Molecular Design

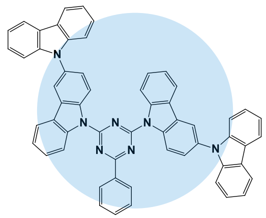
- *Separation of HOMO and LUMO, but rather gentle decrease of HOMO and LUMO distribution for large transition dipole moment.*
- *Use of donor/acceptor units having a high localized triplet state ([3]LE)*
- *Small ΔE_{ST} for short transient time ~μs order*



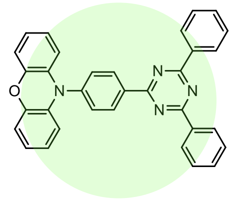
PIC-TRZ
ΔE_{ST} : 0.1eV
λ max : 466nm
EQE : 5.3%
Appl. Phys. Lett., **98**, 83302 (2011)



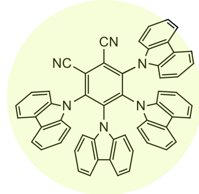
PIC-TRZ2
ΔE_{ST} : 0.01eV
λ max : 505nm
EQE : 14%
Phys. Rev. Lett. **110**, 247401 (2013)



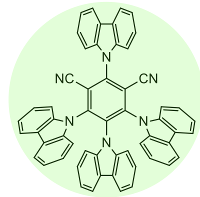
CC2TA
ΔE_{ST} : 0.07eV
λ max : 493nm
EQE : 11%
Appl. Phys. Lett., **101**, 93306 (2012)



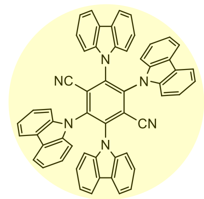
PXZ-TRZ
ΔE_{ST} : 0.0084.eV
λ max : 522nm
EQE : 15.5%
Chem. Com., **48**, 11392 (2012)



4CzPN
ΔE_{ST} : 0.12.eV
λ max : 531nm
EQE : 18%



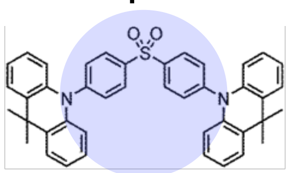
4CzIPN
ΔE_{ST} : 0.01.eV
λ max : 513nm
EQE : 19%



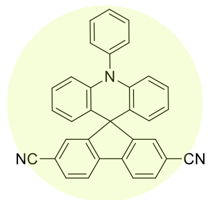
4CzTPN
ΔE_{ST} : 0.06.eV
λ max : 544nm
EQE : 17%

Nature, **492**, 234 (2012)

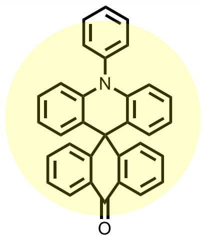
Sulphone



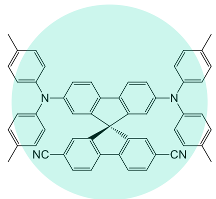
DMAC-DPS
ΔE_{ST} : 0.08eV
λ max : 465nm
EQE : 20%
Nat. Photo. **8**, 326 (2014)



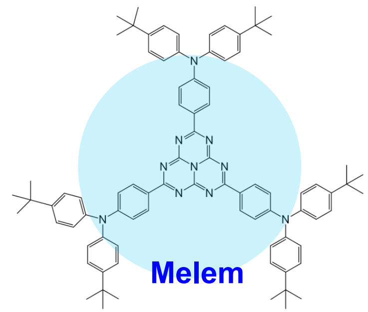
ACRFLCN
ΔE_{ST} : 0.10eV
λ max : 485nm
EQE : 10%
Angew. Chem. **2012**, 51, 11311



Spiro-AN
ΔE_{ST} : 0.025eV
λ max : 495nm
EQE : 16.5%
Chem. Comm. **49**, 10385 (2013)



Spiro-CN
ΔE_{ST} : 0.06eV
λ max : 540nm
EQE : 4.4%
Chem. Com., **48**, 9580 (2012)



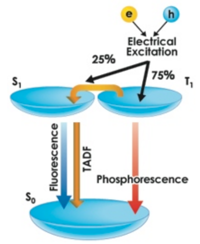
HAP-3TPA
ΔE_{ST} : 0.17.eV
λ max : 610nm
EQE : 17.5%
Adv. Mat.,**25**, 3319 (2013)

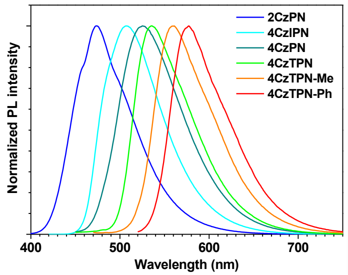
A new route to harvest triplets in OLEDs with fluorescence emitters

TADF based OLEDs

- ✧ *High efficiency up to 100%*
- ✧ *Unlimited molecular design*
- ✧ *Broad spectra due to CT emission*
  (not appropriate for display applications)

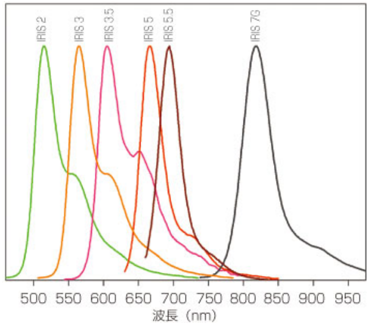
Interamolecular: T. Uoyama et al., Nature, 492, 234 (2012)
Intermolecular: K. Goushi et al., Nature Photo. 6, 253 (2012)

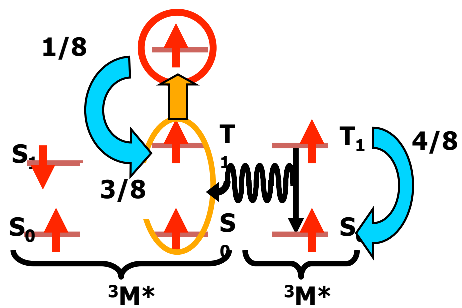




Fluorescence based OLEDs

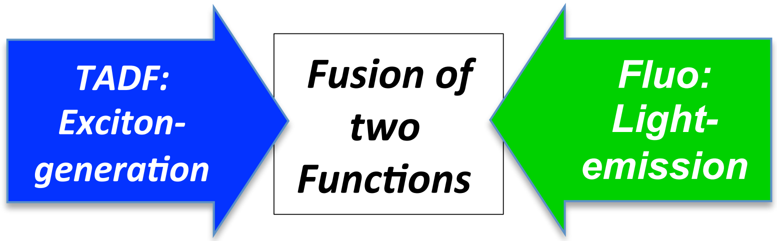
- ✧ *High color purity (narrow spectrum)*
- ✧ *Long lifetimes of operational stability*
- ✧ *Unlimited molecular design*
- ✧ *Theoretical limitation of η_r*
  25% - 62.5% (even TTA process)





TADF as assistant & Fluorescence as emitter

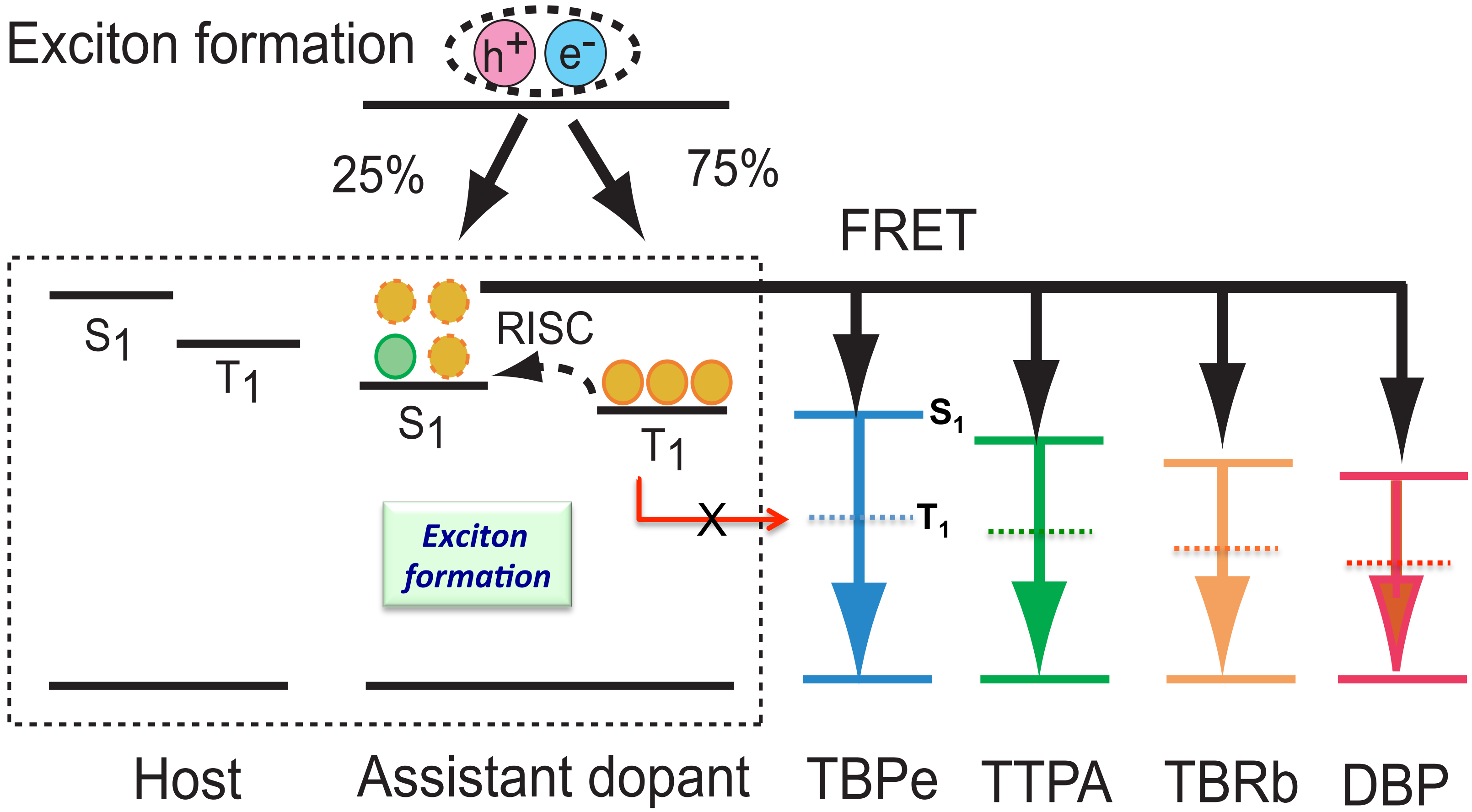
- ✧ *Long lifetimes of operational stability*
- ✧ *High color purity*
- ✧ *Flexibility of material design*
- ✧ *Theoretical limitation of η_r- 100 %*



H. Nakanotani, et al., Nature Comm. 5, 4016 (2014)

TADF as assistant dopant and Fluorescence as emitter in host layer

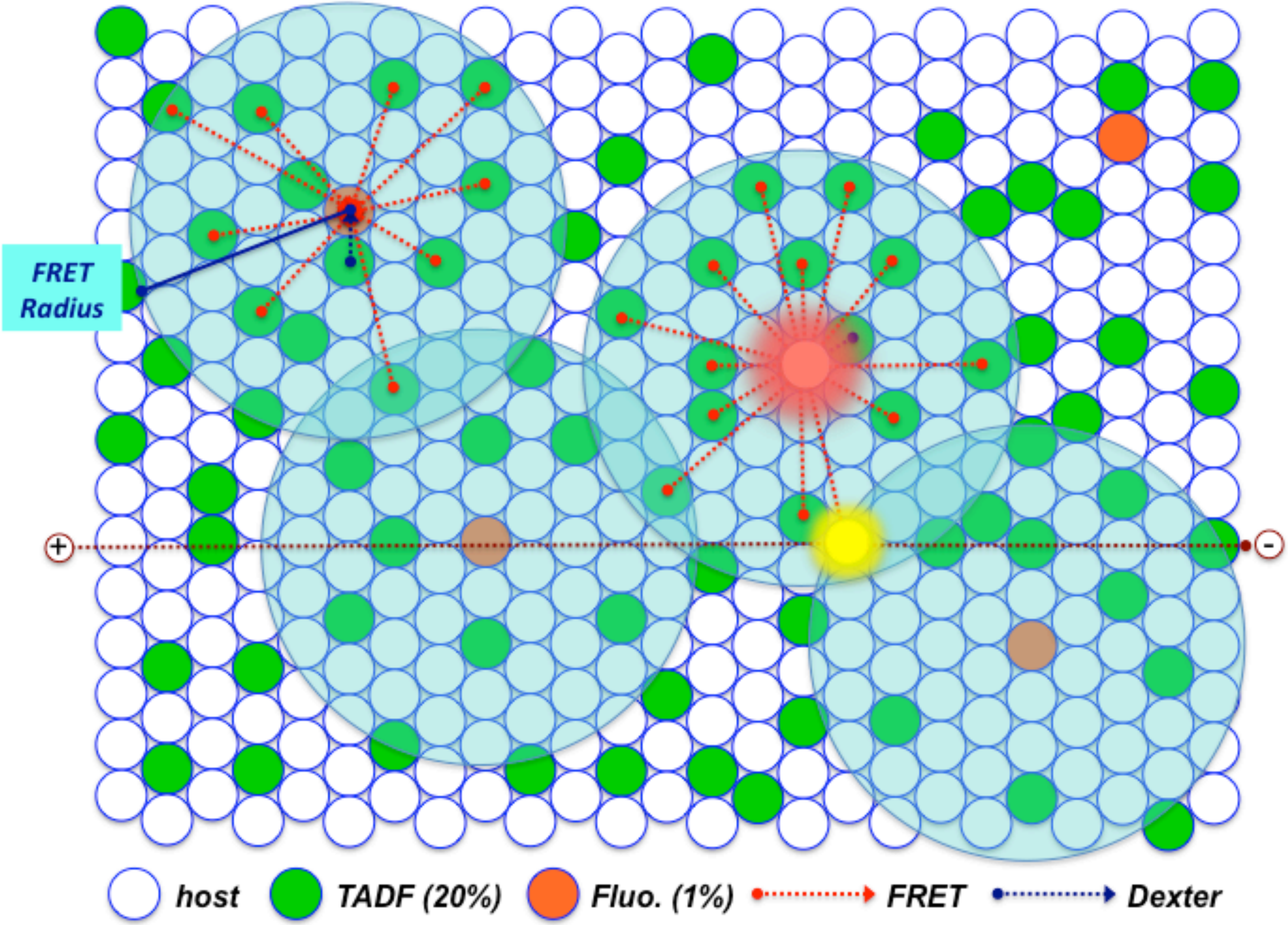
- ✧ ***Minimizing concentration quenching of TADF molecules***
- ✧ ***Efficient FRET but no Dexter transfer***



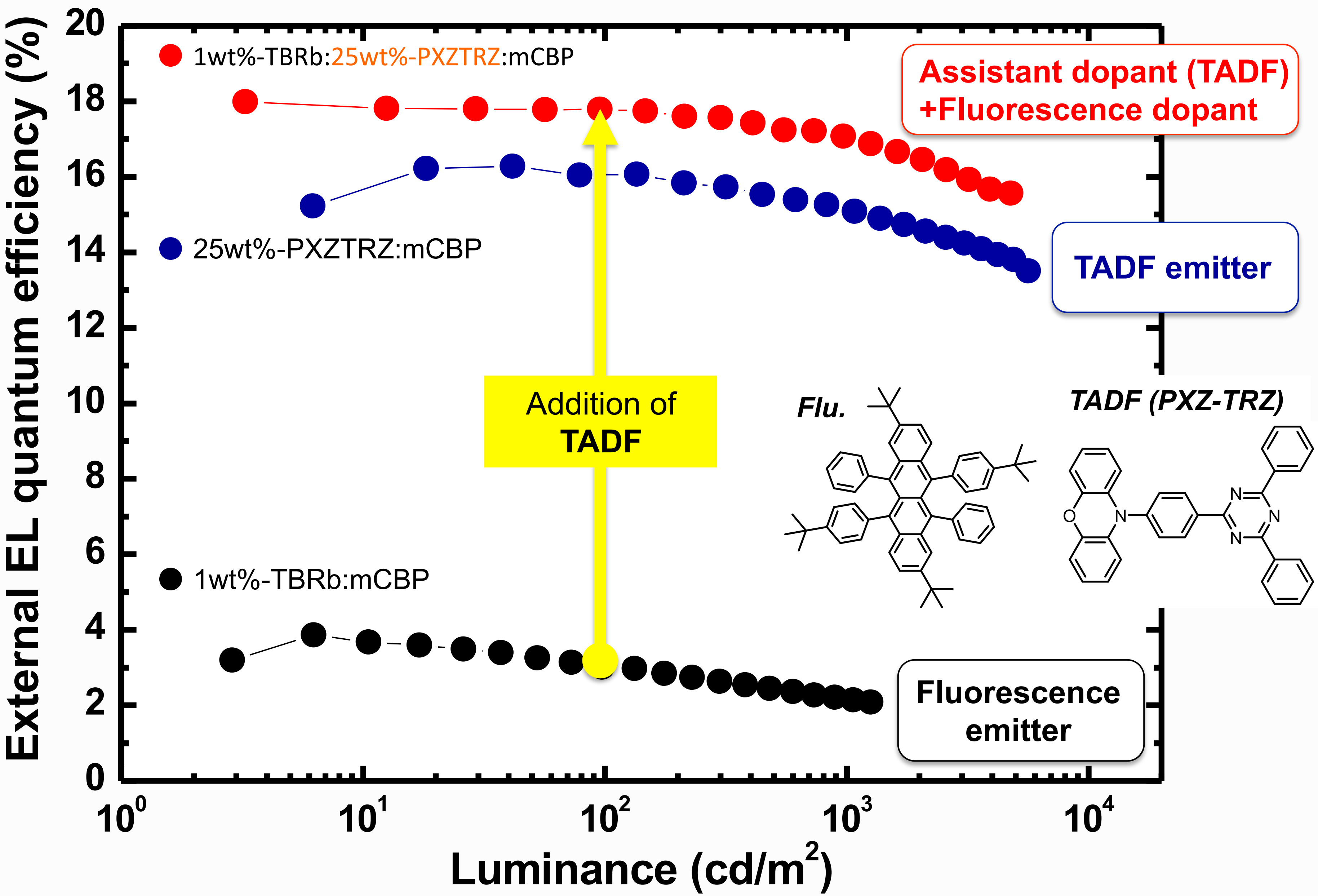
TADF (10-20%) ***Fluorescence emitter (~1%)***

H. Nakanotani, et al, Nat. Commun., 5, 4016, 2014

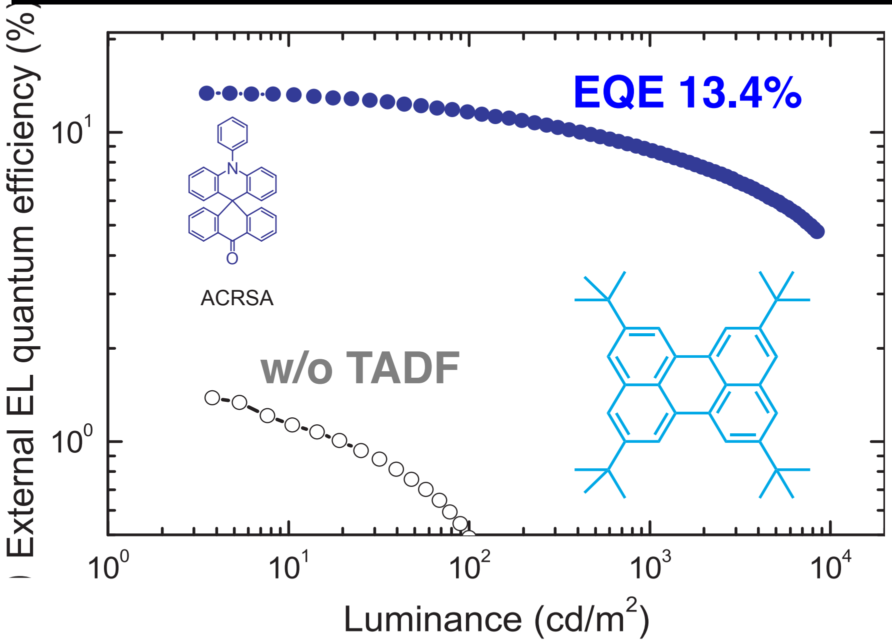
Large chance of FRET and small chance for Dexter between TADF and Fluo.

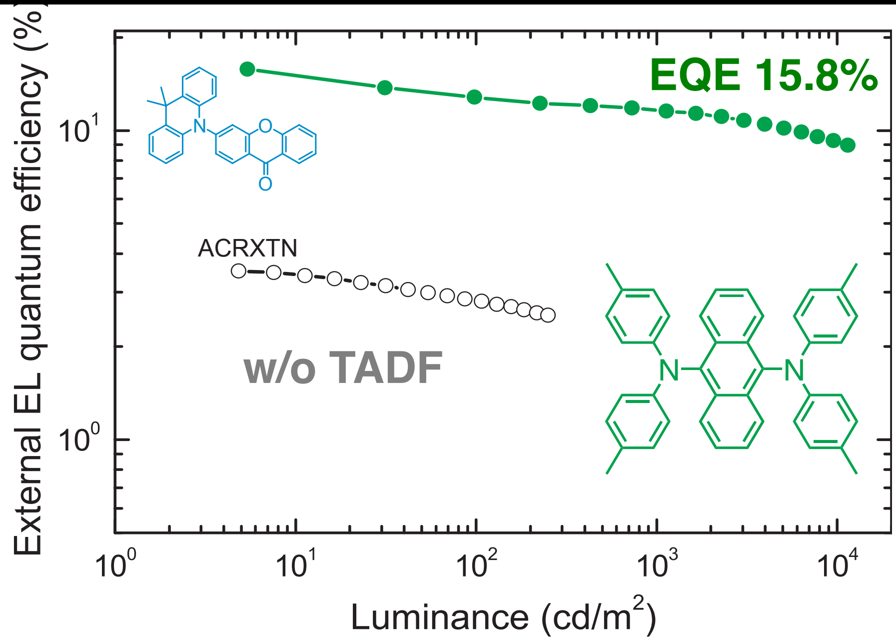


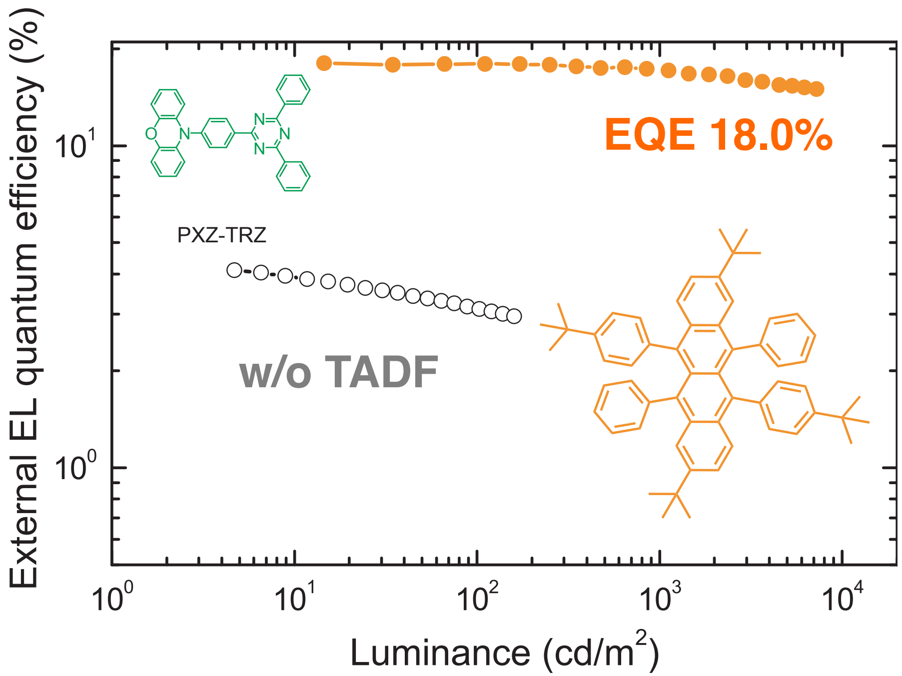
Improved OLED architecture with double doped emitter layer

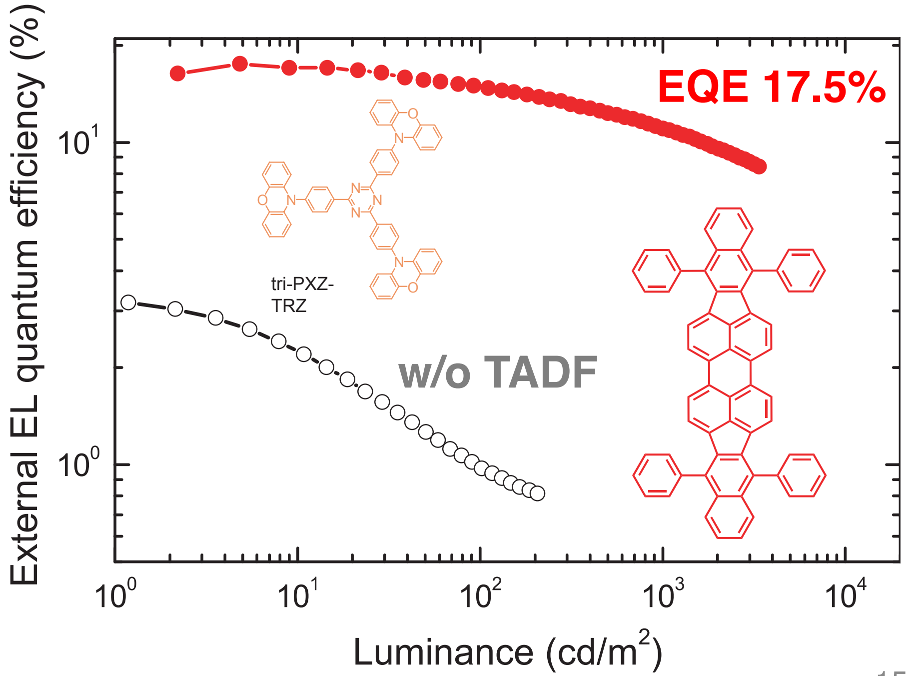


Improved OLED architecture with various emission colors



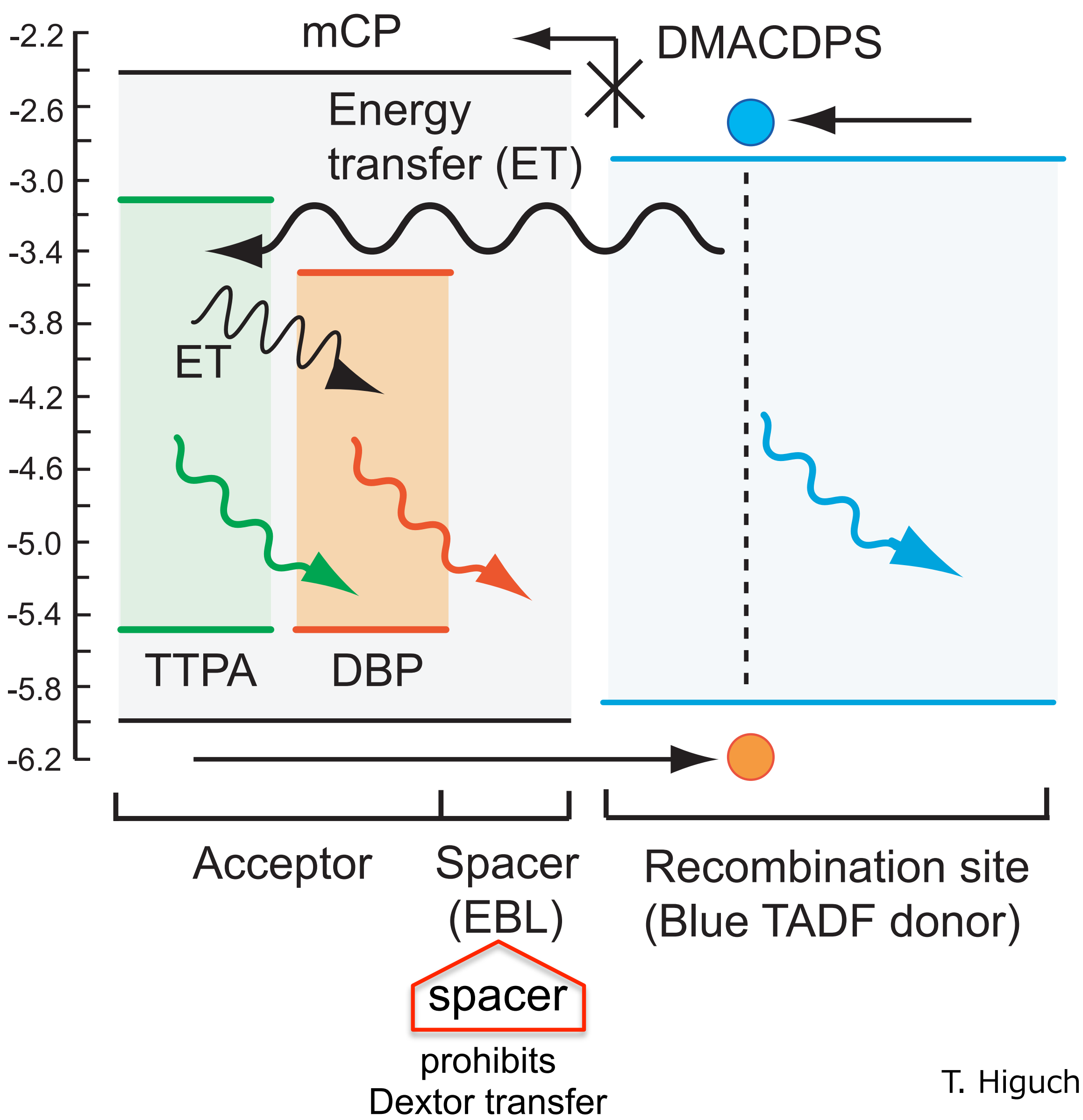




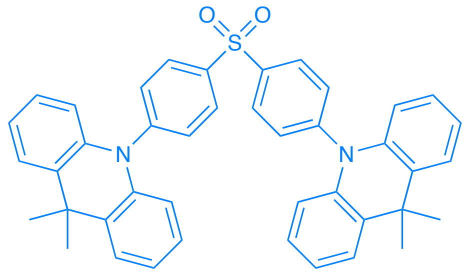


H. Nakanotani, et al, Nat. Commun., 5, 4016, 2014

W-OLED: Spatially separation of D-A layer

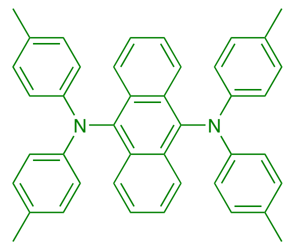


Energy donor (TADF)

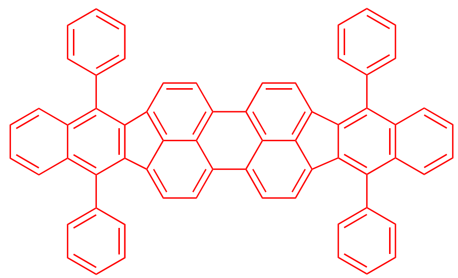


DMAC-DPS

Energy acceptors (Fluo.)



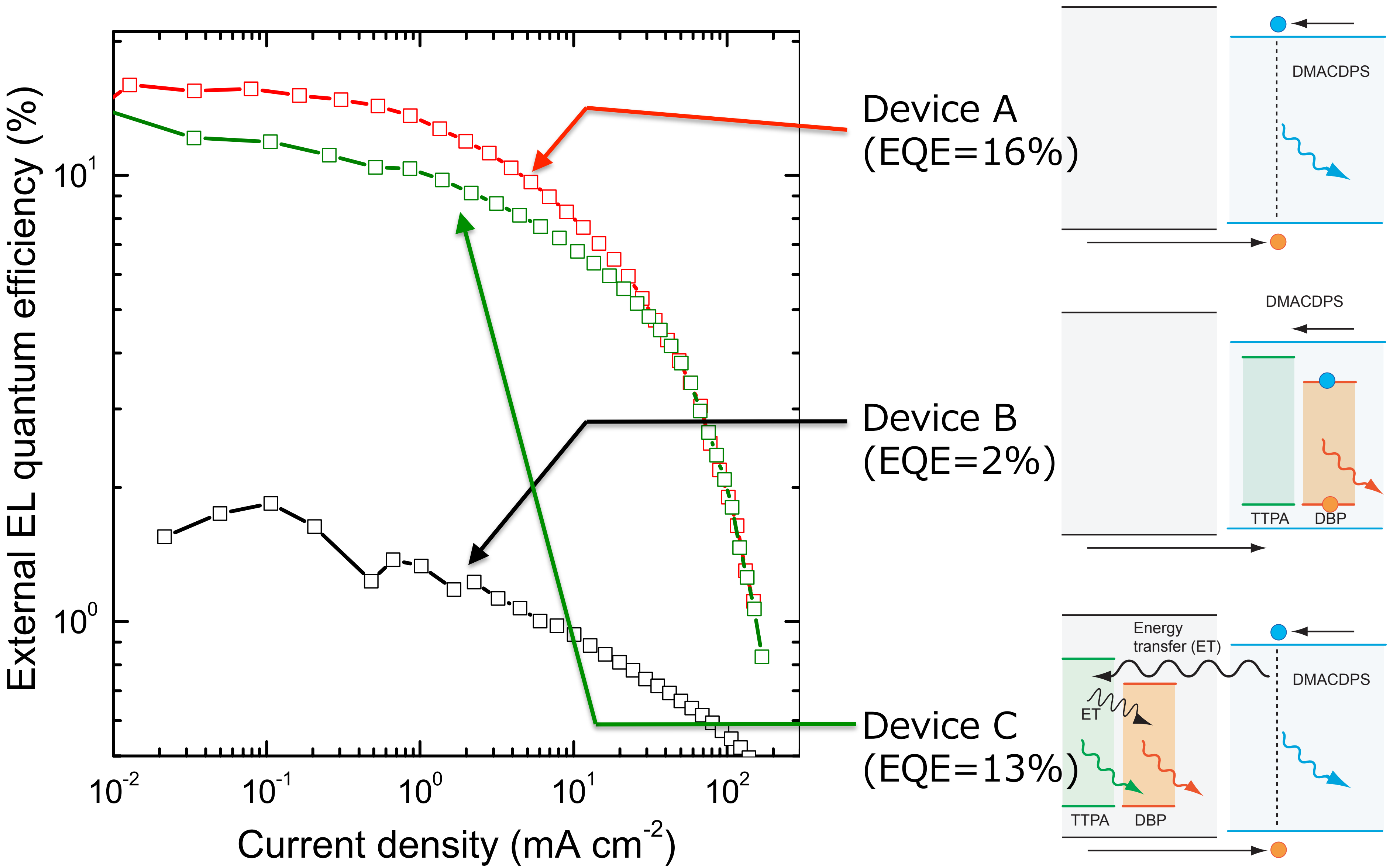
TTPA



DBP

T. Higuchi, H. Nakanotani, C. Adachi (Adv. Mat. in press)

Spatially separation of D-A layer



T. Higuchi, H. Nakanotani, C. Adachi (submitted to Adv. Mat.)

"Promising operational stability of high-efficiency organic light-emitting diodes based on thermally activated delayed fluorescence"

Scientific Reports, 3, 2127 (2013))

H. Nakanotani, K. Masui, J. Nishide, T. Shibata and C. Adachi

SCIENTIFIC REPORTS

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SUBJECT AREAS:

ELECTRONIC DEVICES

ORGANIC LEDS

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APPLIED PHYSICS

Received
15 March 2013

Accepted
17 June 2013

Published
3 July 2013

Correspondence and requests for materials should be addressed to C.A. (adachi@cstf.kyushu-u.ac.jp)

Promising operational stability of high-efficiency organic light-emitting diodes based on thermally activated delayed fluorescence

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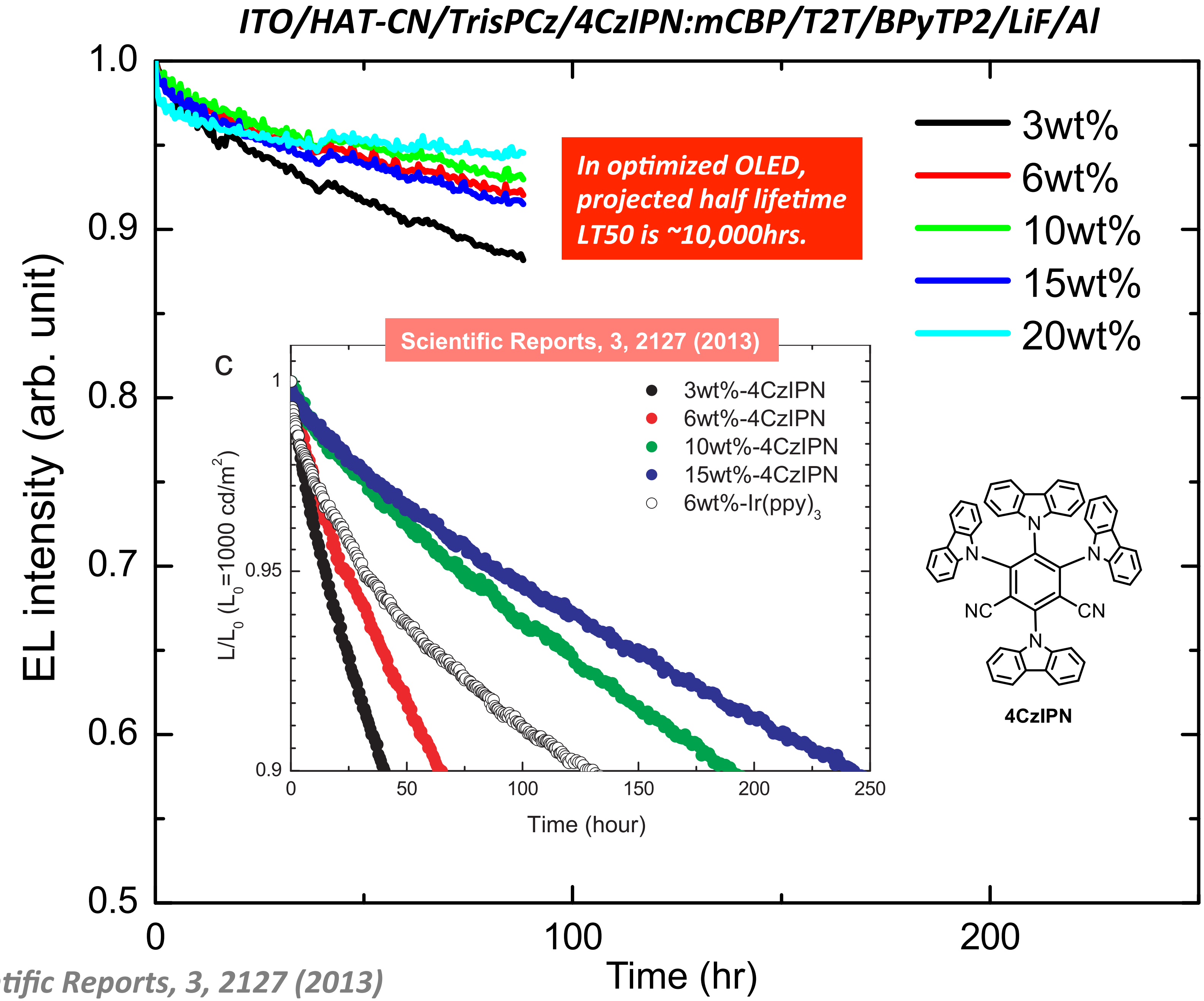
Organic light-emitting diodes (OLEDs) are attractive for next-generation displays and lighting applications because of their potential for high electroluminescence (EL) efficiency, flexibility and low-cost manufacture. Although phosphorescent emitters containing rare metals such as iridium or platinum produce devices with high EL efficiency, these metals are expensive and their blue emission remains unreliable for practical applications. Recently, a new route to high EL efficiency using materials that emit through thermally activated delayed fluorescence (TADF) was demonstrated. However, it is unclear whether devices that emit through TADF, which originates from the contributions of triplet excitons, are reliable. Here we

Improved OLED reliability with 4CzIPN derivatives



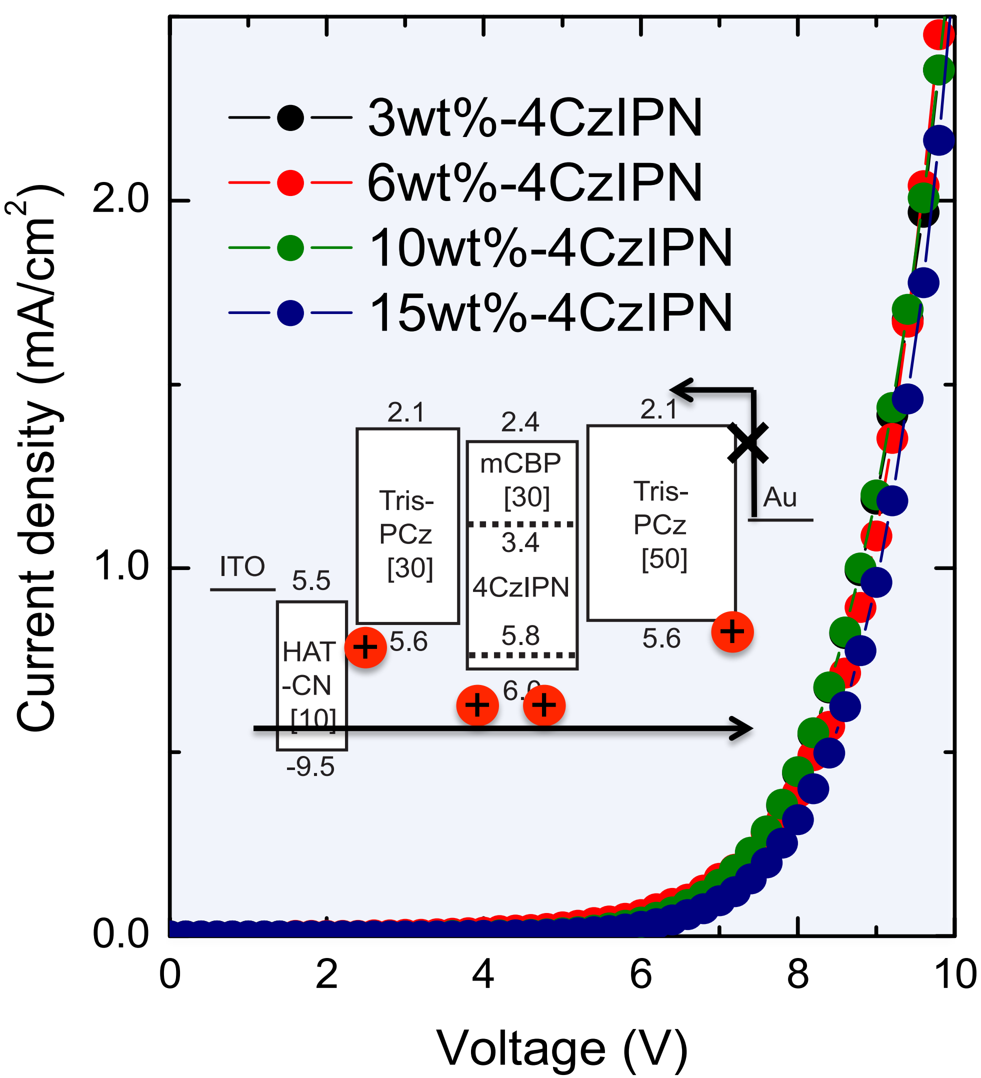
4CzIPN

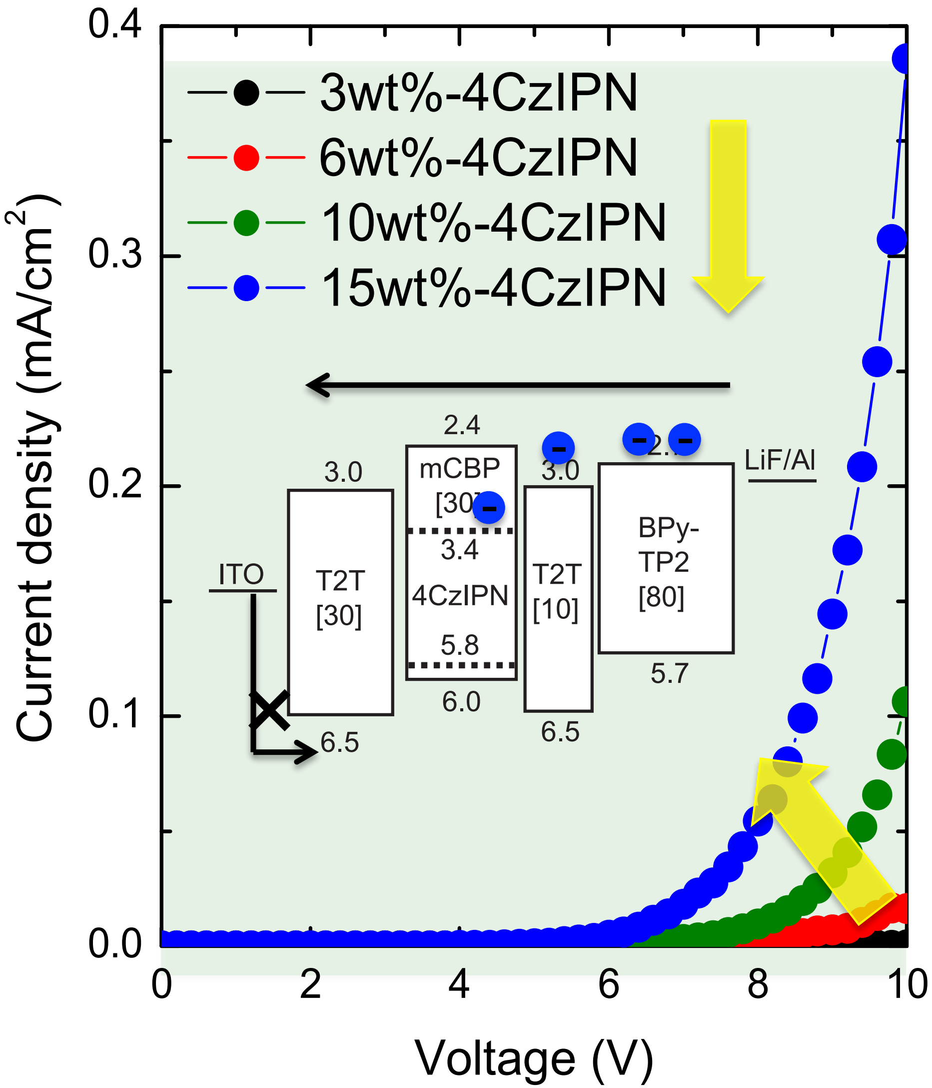
Scientific Reports, 3, 2127 (2013)

Degradation mechanism: J-V in HOD and EOD with different 4CzIPN conc.

Hole only devices
No change in J-V characteristics

Electron only devices
Significant improvement of J-V with increase of 4CzIPN conc.



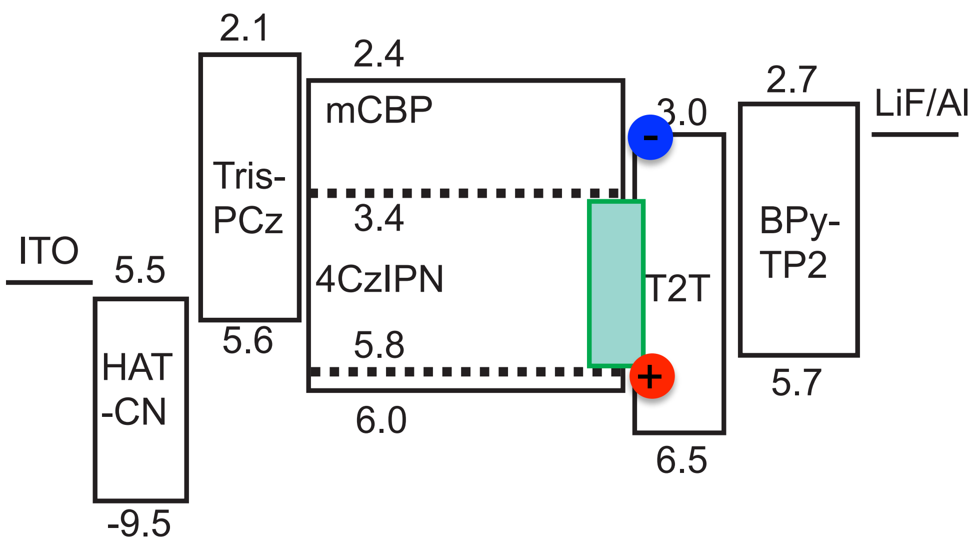


Scientific Reports, 3, 2127 (2013)

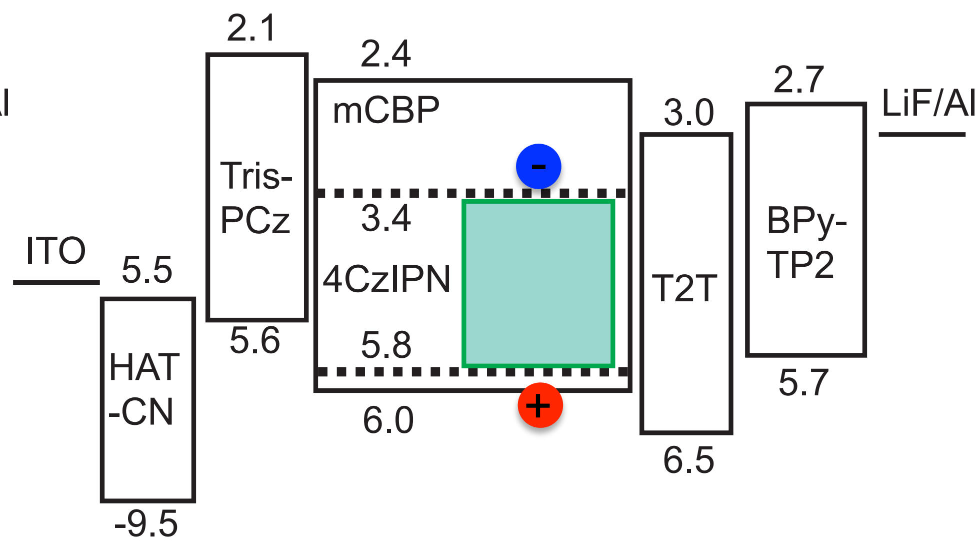
Degradation mechanism: charge accumulation at T2T/EML interface

- ✓ ***Low dopant concentration inhibits electron injection from T2T into EML***
- ✓ ***Higher dopant concentration facilitates electron injection, resulted in expansion of carrier recombination region into EML***

3～6wt%

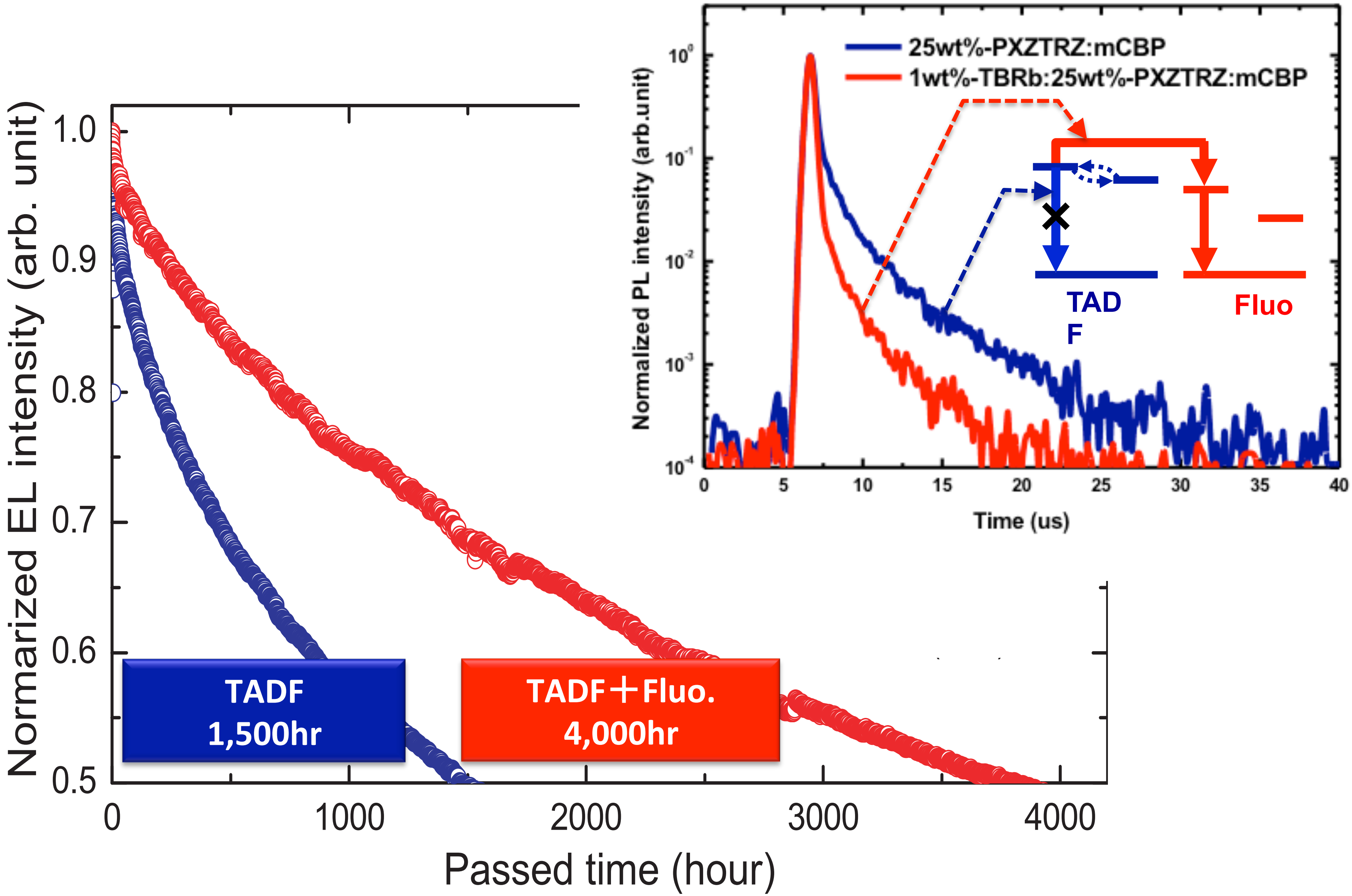


>6wt%



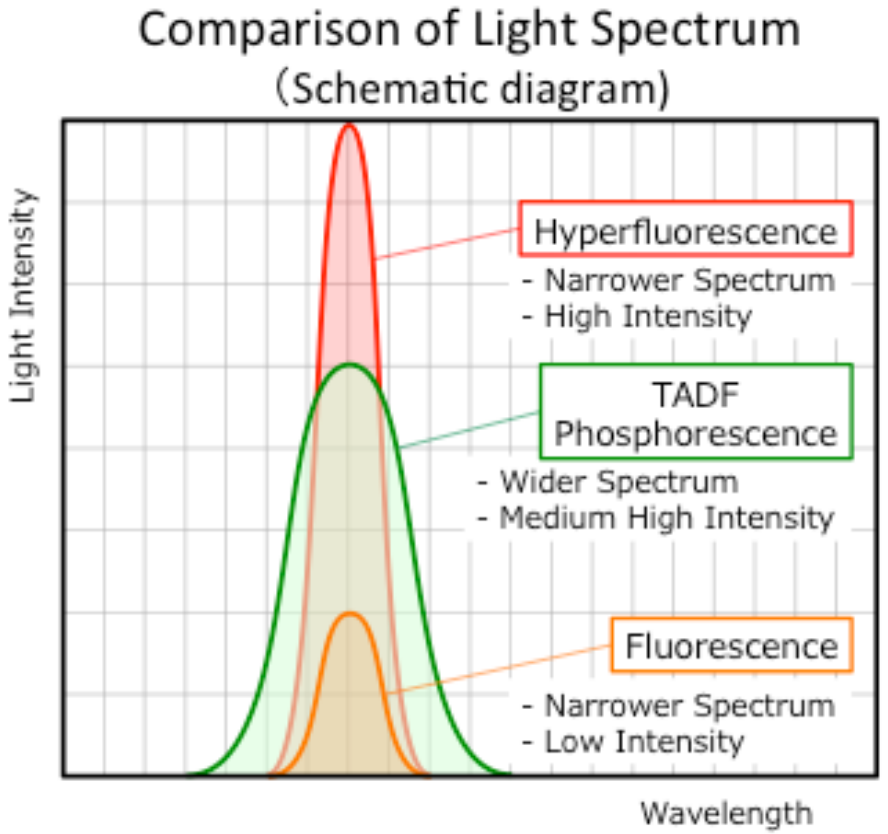
Scientific Reports, 3, 2127 (2013)

Hyperfluorescence :Enhancement of device reliability (> x2.5)

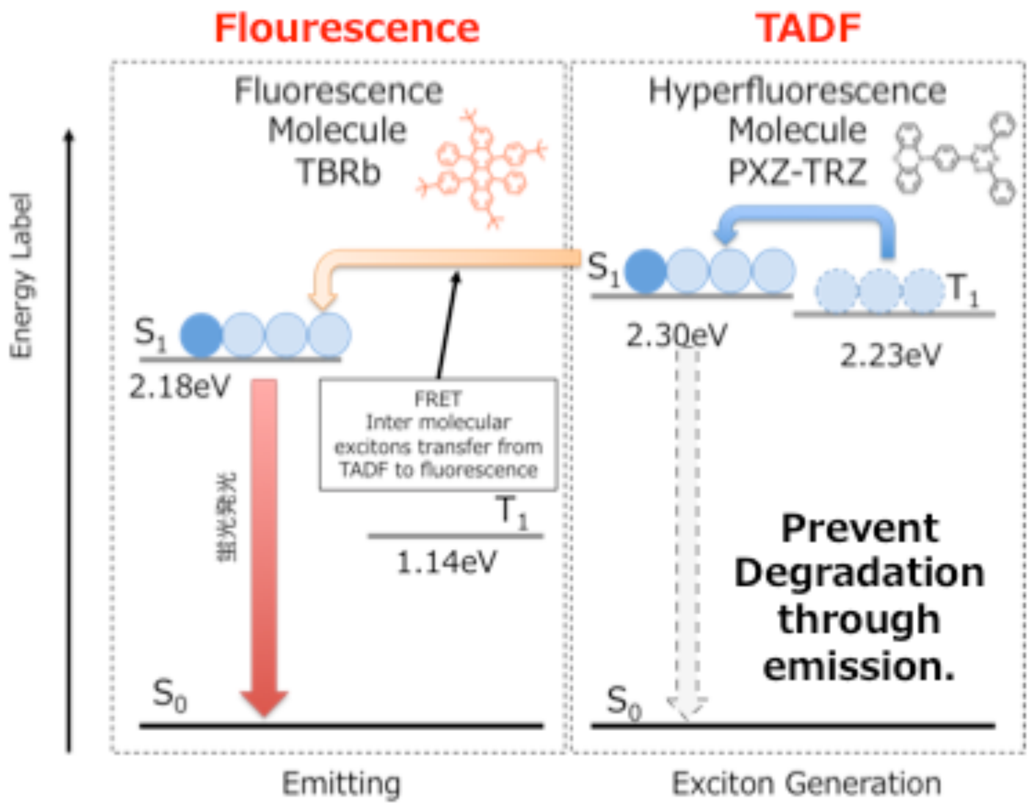


Solution: Assisted Hyperfluorescence with TADF

Superior, high-purity emission color
(Using the features of fluorescent materials)



Decreasing TADF Degradation

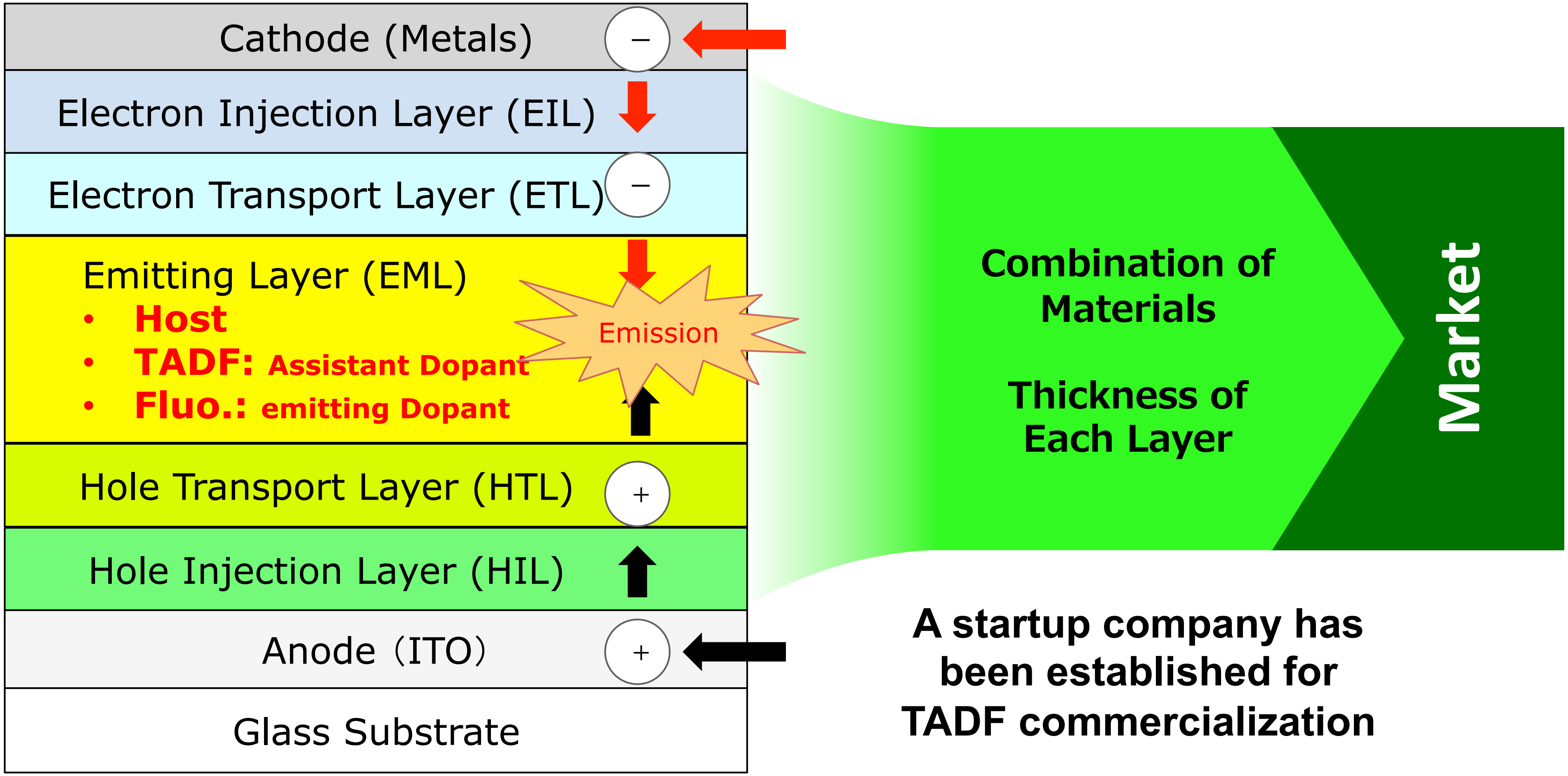


Features
-Exciton generation via TADF (assistant dopant with fluorescent material performing the light-emitting function)
· Achieves high efficiency light-emission with fluorescent material
  Fluorescent materials provide a high-purity light emission color.
· TADF is prevented from rapid deterioration due to the emission process by performing only exciton generation

Effect
High efficiency, high quality emission & *long life* can be achieved through combination of the properties of TADF and fluorescent materials.

Ways to Rapid Commercialization by Achieving Long Life Time

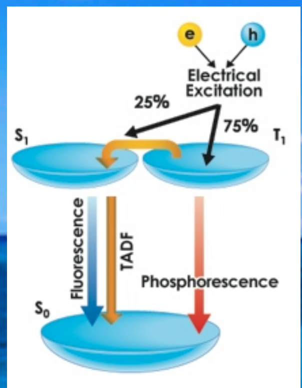
Collaborations with materials & panel manufacturers to optimize devices are the key to rapid commercialization

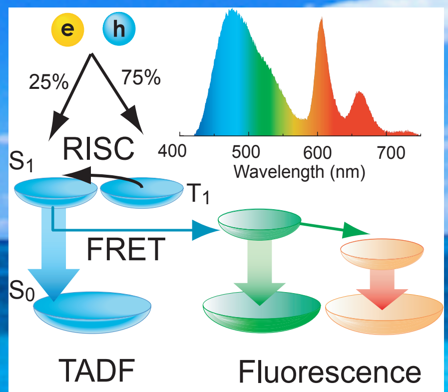


A startup company has been established for TADF commercialization

Summary

- Small ΔE_{ST} realized 100% upconversion from T_1 to S_1, resulted in 100% delayed fluorescence.
- Assistant dopant system realized 100% IQE from fluorescence molecules.
- Device lifetime is significantly enhanced by optimizing peripheral materials.
- Rapid upconversion shorter $\tau_{T \rightarrow S}$ less than 1μs will be expected for further development of high performance TADF and lasers.





Acknowledgement

OPERA Research Team in Kyushu Univ. and collaborators

FIRST PROGRAM *2010-2014*

exciton JST ERATO *2014-2019*

This work was supported by Funding Program for World-Leading Innovation R&D on Science and Technology (FIRST), WPI and JST ERATO.

- ***Supervisors***
  Prof. T. Yasuda
  Prof. K. Goushi
- ***SnF_2OEP***
  A. Endo, A. Takahashi
- ***PIC-TRZ, PIC-TRZ2***
  K. Sato, H. Miyazaki, K. Yoshimura, A. Kawada
- ***Cz-TRZ***
  SY. Lee, S. Hirata
- ***PXZ-TRZ***
  H. Tanaka. K. Shizu, J. Lee
- ***HAP-3TPA***
  Jie Li, T. Nakagawa, James MacDonald, K. Ueno (CSIRO), Q. Zhang, H. Nomura
- ***Phthalonitrile***
  T. Uoyama, K. Shizu, H. Nomura
- ***4CzIPN (Reliability)***
  H. Nakanotani, K. Masui, J. Nishida, T. Shibata
- ***Anthraquinones***
  Q. Zhang, H. Kuwabara
- ***Blue TADF***
  Q. Zhang, BoLi
- ***Double doping of TADF and Fluo.***
  H. Nakanotani, T. Higuchi, T. Furukawa
- ***Special thanks to collaborators***
  Profs. Kaji (Kyoto U), Murata (JAIST), Ishii (Chiba U), Orita (Okayama U), Takimiya (Hiroshima U), Naito (Osaka Pref. U.), Matsumoto (Osaka City U.), Ueda (Kobe U), Mizuno (Waseda U.), Sato (Nagaoka), Kawai (NAIST), Ueno (CSIRO)

JDI, TEL, Panasonic, Mitsbishi Ryon, Tokai Rubber, Hirata, Daiden, Toshiba, Hodogaya Chemical, NSCC, Nippon Kayaku